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Band gap tuning of amorphous Al oxides by Zr alloying

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The optical band gap and electronic structure of amorphous Al-Zr mixed oxides with Zr content ranging from 4.8 to 21.9% were determined using vacuum ultraviolet and X-ray absorption spectroscopy. The light scattering by the nano-porous structure of alumina at low wavelengths was estimated based on the Mie scattering theory. The dependence of the optical band gap of the Al-Zr mixed oxides on the Zr content deviates from linearity and decreases from 7.3 eV for pure anodized Al₂O₃ to 6.45 eV for Al-Zr mixed oxides with a Zr content of 21.9%. With increasing Zr content, the conduction band minimum changes non-linearly as well. Fitting of the energy band gap values resulted in a bowing parameter of ~ 2 eV. The band gap bowing of the mixed oxides is assigned to the presence of the Zr *d*-electron states localized below the conduction band minimum of anodized Al₂O₃. Published by AIP Publishing. [<http://dx.doi.org/10.1063/1.4961941>]

In recent years, many efforts have been dedicated to the development of high- κ gate dielectric materials for advanced metal-oxide semiconductor (CMOS) devices. Aluminum oxide (Al₂O₃) is one of the leading candidates to replace ultrathin SiO₂ gate dielectrics for future CMOS technologies.^{1,2} Al₂O₃ has a considerably larger dielectric constant than SiO₂,³ resulting in reduced gate leakage currents for layers of comparable thicknesses.¹ Fabrication of ultra-thin pure or alloyed Al mixed oxides by anodic oxidation of Al or Al alloys, respectively, is one of the most cost-effective methods and it has been implemented at large industrial scale. Theoretical predictions have shown that alloying of Al₂O₃ with transition metals (TM) can result in a larger dielectric constant without significant reduction of the band gap of Al₂O₃. The possibility of tuning the structural and optical properties of Al₂O₃ by varying the alloying composition will broaden the range of materials available from pure oxides. Several studies were dedicated to understanding the electronic properties and changes in the band gap of amorphous anodic Al₂O₃ upon alloying.^{3–5} Theoretical studies based on density functional theory have shown that transition metal atoms, such as Zr atoms present in Al sites, introduce localized *d*-electron states below the conduction band (CB) of Al₂O₃.⁶ Experimental determination of the band gap energy of Zr-alloyed Al₂O₃ is not readily available because ultraviolet and visible measurements are limited to energies below 6 eV due to the absorption of air. For a comprehensive electronic structure study, vacuum ultraviolet (VUV) spectroscopy is required to probe the valence-to-conduction band transitions in most high- κ materials of large band gap.³

In this letter, the band gap of anodic Al-Zr mixed oxide films was determined by vacuum ultraviolet spectroscopy (VUV), while the unoccupied conduction band states of the

alloyed oxide films were investigated by X-ray absorption spectroscopy (XAS). The dependence of the energy gap of the anodic Al oxide films on the Zr alloying will be discussed.

Thin metallic films of Al-Zr alloys were deposited by DC magnetron sputtering on double-side polished sapphire substrates. Two Al targets (99.99%) and two Zr targets (99.9%, Hf being the primary impurity) were used for co-sputtering the Al-Zr alloys. The film composition was adjusted by changing the relative power on the Al and Zr sputter targets, keeping the total power constant, while the sputtering time was appropriately set in order to deposit films of similar thickness. The anodization was performed in a dual-electrode cell, where an Al-Zr film on sapphire served as the anode and a Pt mesh served as the cathode. All films were anodized in 20% sulphuric acid at a constant voltage of 20 V at 18 °C. The anodization was stopped when the observed current density was stabilized at 0.1 mA/cm². The films were not sealed after anodizing, such that the anodized layer consists of a self-organized hexagonal porous structure with open pores.⁷ The Zr content in the as-sputtered films was determined by Rutherford Backscattering Spectrometry (RBS). The thickness of the resulting anodized films, measured by profilometry and cross section SEM, was varying between 180 to 380 nm. Vacuum ultraviolet (VUV) spectroscopy measurements were carried out in the transmittance mode in the energy range from 4.13 to 9.18 eV (300–135 nm) at the AU-CD beamline of the ASTRID2 Synchrotron Light Source, Aarhus University, Denmark in a N₂ purged chamber to avoid absorption of the UV light by air molecules. A baseline measurement of a clean sapphire substrate was acquired before and after each sample measurement. The resolution over the measured spectra range was constant with a value of 0.45 nm. The XAS measurements at the oxygen K-edge were carried out at the X-Treme beamline⁸ at the Swiss Light Source, Paul Scherrer Institut, Switzerland. The

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measurements were performed in the total electron yield mode using circular in-plane polarization. The energy scans were recorded with the monochromator and insertion device moving continuously during scanning.⁹ This approach helps to reduce the surface charging, which unavoidably occurs on insulating samples. After background subtraction, all spectra were normalized to unity at 50 eV above the oxygen K-edge.

The Zr content in the as-deposited films was estimated by Rutherford Backscattering Spectrometry (RBS) (see Table I). The X-ray Absorption Near-Edge Spectroscopy (XANES) spectra at the O K-edge are shown in Fig. 1(a). The O K-edge spectra reflect the unoccupied O 2p (conduction band) states of the anodized Al-Zr films. A pre-peak feature located below the absorption threshold of the O K-edge (between 530 and 534 eV) is evident in all spectra. This low photon energy feature at the O K-edge is assigned to O 2p states hybridized with Zr 4d states.¹⁰ The appearance of a pre-peak feature upon Zr alloying suggests that Zr replacing Al sites introduces localized Zr *d*-electron states below the conduction band minimum (CBM) of aluminum oxide,⁶ which is in agreement with theoretical predictions by density functional theory.¹¹ As it can be observed in Fig. 1(a), the intensity of the pre-peak increases monotonically with increasing Zr content from 4.8% to 15.8% due to a greater number of unoccupied Zr 4d electron states available for mixing with the O 2p states. However, the intensity of the pre-peak corresponding to a Zr content of 21.9% no longer follows a linear increase and is comparable with that of Zr 15.8%. The apparent “loss” in intensity may indicate a partial change in the local structure around oxygen atoms. The X-ray diffraction pattern of the anodized Al-Zr films (Al-Zr mixed oxides) reveals that the all oxide films are amorphous (not shown). However, for the Al-film with a Zr content of 21.9%, a peak associated with the monoclinic ZrO₂ was observed. Therefore, the change in oxygen pre-peak edge intensity for a high Zr content can be explained by the fact that Zr is no longer fully replacing Al atoms and it can also be found in a mixed coordination state. The XAS spectra were used to determine the conduction band minimum (CBM) of alumina by extrapolating the leading edge of the XANES spectra to the baselines. The O K-edge shifts towards lower energy with increasing Zr content. The CBM shifts non-linearly with Zr content, as shown in Fig. 1(b).

The band gap of pure anodic amorphous Al₂O₃ and Al-Zr mixed alloy oxides was determined from vacuum

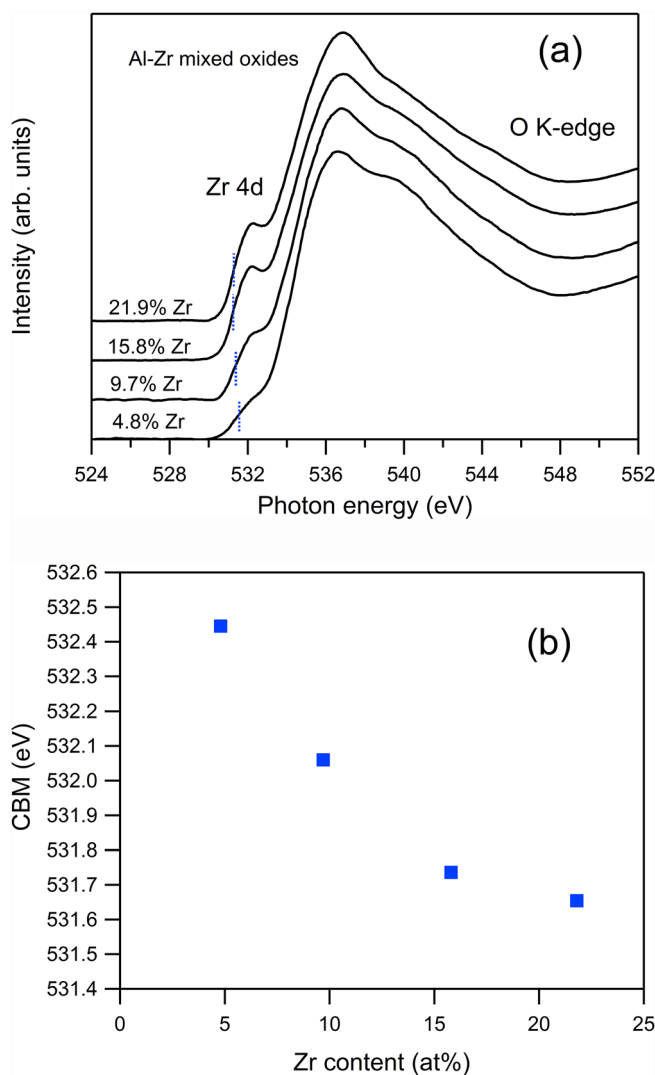


FIG. 1. (a) XAS spectra at the O K-edge of Al-Zr mixed oxides with Zr contents of 4.8, 9.7, 15.8 and 21.9%; (b) Conduction band minimum (CBM) as a function of Zr content. The energy resolution was about 0.08 eV.

ultraviolet spectroscopy (VUV). The VUV transmittance spectra of the anodic oxide films on sapphire are shown in Fig. 2(a). The transparency of the oxide layers decreases markedly at short wavelengths, i.e. below 200 nm. Amorphous Al₂O₃ shows a distinct absorption slope below 170 nm. Upon Zr alloying, the absorption edge shifts to higher wavelengths (lower photon energy). As mentioned earlier, the anodized layer consists of a self-organized hexagonal porous structure with open pores⁷ with a typical diameter of ~13 nm and porosity up to 14%.¹² It is thus useful to discuss the nature of the sharp decrease in transparency of the mixed oxide layers with consideration of porosity (light scattering by nano-pores) and absorption contributions in alumina. Taking into account the size of the nanopores and the pore volume fraction of the oxide layers, we have estimated that the losses in transmittance due to scattering by nano-pores in alumina are negligible (see [supplementary material](#)). Since the size of the nano-pores and the volume fraction of the pores do not depend on the composition of the samples, but rather on the anodization voltage (which was kept constant for all samples), light scattering of the pores has an insignificant contribution to the transmission losses.

TABLE I. Experimentally determined VUV optical band gap of anodized Al₂O₃ and Al-Zr anodized alloys with the Zr content varying from 4.8% to 21.9%. Reference data: optical band gap of single crystal γ -Al₂O₃³ and anodized ZrO₂.¹⁹

Specimens	Band gap energy (eV)
Single crystal γ -Al ₂ O ₃	8.7
Amorphous anodized Al ₂ O ₃	7.3
Anodized ZrO ₂	4.75
Al-Zr mixed oxides	
4.8% Zr (~340 nm) ^a	7.06
9.7% Zr (~330 nm)	6.8
15.8% Zr (~240 nm)	6.6
21.9% Zr (~340 nm)	6.45

^aThe thickness of the anodized films is given in parenthesis.

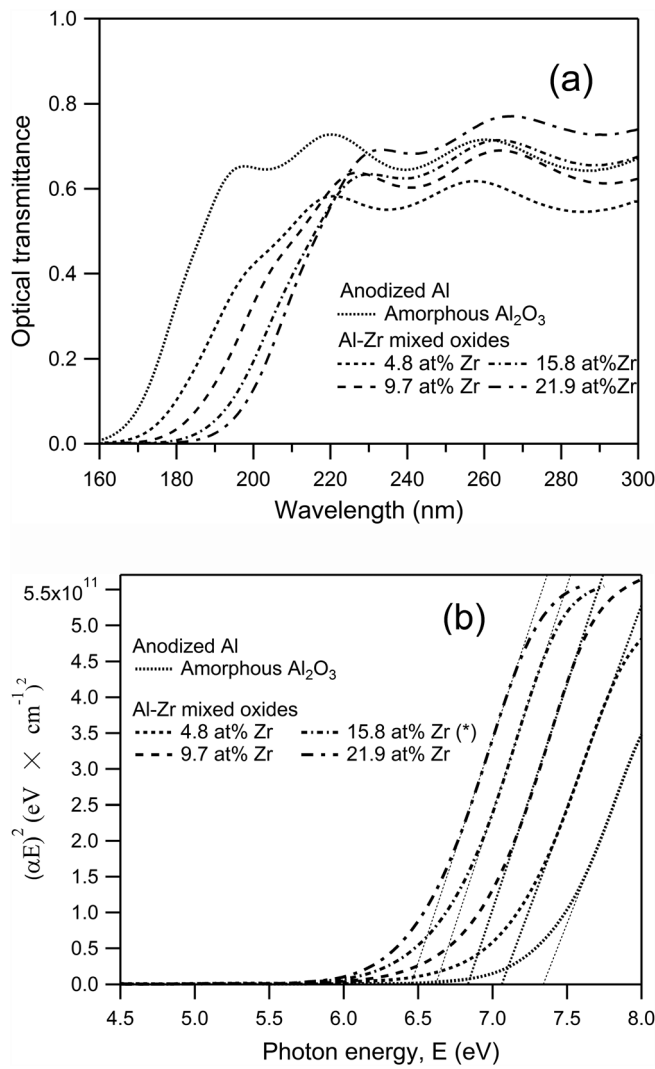


FIG. 2. (a) Vacuum ultraviolet (VUV) optical absorption coefficient of amorphous anodic Al_2O_3 and Zr-Al mixed oxides as a function of wavelength; (b) Plots of $(\alpha h\nu)$ versus $(h\nu)$ for the Zr-Al mixed oxide films with Zr contents of 4.8, 9.7, 15.8 and 21.9%. The plot (*) was divided by half for an easy visualization of the data.

Changes in the refractive index of the Al-Zr mixed oxides by 5% with Zr content with respect to the pores leads to only about 1.5% variation in transmittance of the anodic layer. For the calculation of the band gap, we have therefore assumed that the incident light is either transmitted or absorbed, with scattering being negligible.¹³ The absorption coefficient for optical direct transitions is related to the incident photon energy by the relation^{14,15}

$$(\alpha E)^2 = (E - E_{\text{opt}}), \quad (1)$$

where α , E , and E_{opt} are the absorption coefficient, photon energy, and optical band gap, respectively. By replotting the data shown in Fig. 2(a) according to Eq. (1), optical band gap E_{opt} was determined by extrapolating the linear dependence of $(\alpha E)^2$ to zero. This plot is shown in Fig. 2(b) for pure Al_2O_3 and Zr-alloyed Al_2O_3 with Zr content varying from 4.8% to 21.8%. The determined optical band gap values are also summarized in Table I. Amorphous anodized Al_2O_3 has a direct band gap of 7.3 eV, which is about 1.4 eV lower than the crystalline counterpart, i.e., 8.7 eV for single

crystal $\gamma\text{-Al}_2\text{O}_3$ ³ (see Table I). A lower optical band gap of amorphous oxide compared to its crystalline counterpart can be associated with the different band structure resulting from a broad distribution of bond angles and distances.^{4,5} In fact, it was shown that the band gap of Al_2O_3 can be increased by ~ 1 eV from an amorphous to a crystalline structure by annealing induced crystallization.¹⁶ Filatova *et al.*¹⁷ have suggested that the variation in the energy gap between amorphous and crystalline Al_2O_3 ($\alpha\text{-Al}_2\text{O}_3$) is due to a shift of the bottom of the conduction band. The optical band gap of anodic amorphous Al_2O_3 decreases upon Zr alloying from 7.06 eV, corresponding to a Zr content of 4.8%, to 6.45 eV where the Zr content is 21.9%. A reduction of the band gap of anodic Al_2O_3 was also reported for other transition metal-alloyed Al_2O_3 , such as Nb^{4+} and Ti^{3+} . On the other hand, alloying of Al_2O_3 with Sc and Y was shown to induce little change in the band gap of Al_2O_3 .⁶

The electronic structure of Al_2O_3 is well understood.¹⁴ The top of the valence band (VB) arises from O 2p orbitals, while the bottom of the conduction band (CB) arises from delocalized Al 3s empty states and Al 3p states higher up in the CB. The energy gap in Al_2O_3 is due to electronic transitions from O 2p to Al 3s orbitals.¹⁴ Band-gap state analysis of the Al-Zr mixed oxides suggests the formation of an impurity band below the CBM of Al oxide upon Zr alloying. Hence, band to band transitions in Al-Zr mixed oxides can be associated with transitions from the populated O 2p-states at the top of the VB to the empty Zr 4d-electron states located below the CBM.

In order to describe the compositional dependence of the band gap of the Al-Zr mixed oxides, we have used the standard bowing equation, which can be described as¹⁸

$$E_g(\text{Al} - \text{Zr mixed oxides}) = (1 - x)E_g(\text{Al}_2\text{O}_3) + xE_g(\text{ZrO}_2) - bx(1 - x), \quad (2)$$

where $E_g(\text{Al}_2\text{O}_3)$, $E_g(\text{ZrO}_2)$, and $E_g(\text{Al} - \text{Zr mixed oxides})$ are the band gaps of Al_2O_3 , ZrO_2 , and Al-Zr mixed oxides, respectively. The parameter b is known as the *bowing parameter* and represents the deviation of the band gap from linearity. The variation of the band gap as a function of alloying content is plotted in Fig. 3, while the dashed line describes the fitting according to Eq. (2). The fitting was done using the direct band gap of anodic amorphous Al_2O_3 of 7.3 eV and of anodic amorphous ZrO_2 of 4.8 eV.¹⁹ Fitting of the experimental data with the parabolic function results in a bowing parameter value of $b = 2 \pm 0.2$ eV. The determined bowing parameter is lower than the one reported for anodic Al-Nb mixed oxides, i.e., 4.3 eV.⁴ Typically, a small value of the bowing parameter, and thus a small deviation from the linearity of the band gap of alloys, can indicate a good miscibility of the alloys, such as $b = 0.1$, as estimated from polycrystalline CZGTS (Se) alloys.²⁰ A larger value of the bowing parameter, such as the one determined here and also reported for Al-Nb mixed oxides, indicates that the randomness in the alloys strongly influences the energy gap of the alloys.

The compositional dependence of a band gap can originate from three distinct contributions: (i) change in the band structure due to change of the lattice constant upon alloying, (ii) modified atom positions with the internal structural

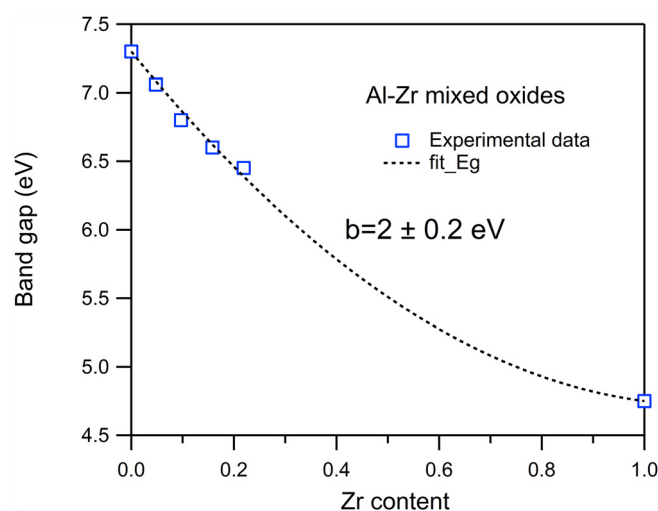


FIG. 3. Optical band gap energy (E_{opt}) estimated from the VUV absorption spectra as a function of Zr content, x . The dotted line represents band bowing fitting according to Eq. (2) resulting in a bowing parameter of (b) of 2 ± 0.2 eV.

relaxation of the bond lengths of the alloys, and (iii) charge exchange owing to different electronegativity of alloyed systems resulting in localized energy levels below the CBM.²¹ The bowing behaviour observed in the Al-Zr mixed alloys can be attributed to charge exchange resulting in localized d-electron states below the band gap minimum of alumina, since all anodic films are amorphous. This is also supported by the XAS findings, which reveal the presence of Zr d-electron states below the CBM of alumina alloys. Obviously, Zr-alloying in the alumina leads to a redistribution of the valence band/conduction band levels while the non-linear shift of the CBM with increasing Zr content supports the existence of a bowing behaviour. At a low Zr content (4.8%) the Zr d-electron states are localized below the CBM of alumina. The high degree of localization was theoretically predicted for Al-Zr mixed oxides with Zr content in alumina of 6.5 at. %.¹¹ Thus, the impurity band in alumina persists at a Zr content of 4.8%. However, more strongly localized Zr 4d states exist in 15.8% Zr-alloyed Al_2O_3 compared to 21.8% Zr-alloyed Al_2O_3 . This indicates that for a large Zr content (21.8%), the Zr d-electron states merge with the extended states in the conduction band. It is thus expected that the conduction band minimum moves continuously with increasing concentration according to Eq. (2).

In summary, we have experimentally determined the optical band gap of Al-Zr mixed oxides by vacuum ultraviolet spectroscopy (VUV). Optical losses due to light scattering by the nano-porous structure of alumina at UV wavelengths

were estimated to be negligible. The Zr-Al mixed oxides have a band gap that varies, decreasing from 7.06 eV to 6.45 eV with increasing Zr content from 4.8% to 21.9%. The optical band gap decreases monotonically with increasing Zr content, showing a band bowing behaviour with a bowing parameter of 2.2 eV. The band bowing in Zr-Al mixed oxides arises from the non-linear shift of the conduction band minimum with the Al content.

See [supplementary material](#) for the calculation of the transmission losses in alumina due to light scattering by nano-pores.

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